

# PATENT SPECIFICATION

NO DRAWINGS

1,045,577



1,045,577

Date of Application and filing Complete Specification: Oct. 15, 1963.

No. 40609/63.

Application made in Germany (No. D40062 IVc/221) on Oct. 16, 1962.

Complete Specification Published: Oct. 12, 1966.

© Crown Copyright 1966.

Index at acceptance:—C3 P(2C4A, 2C8B, 2C8C, 2C13A, 2C13B, 2C20D1, 2C20D3, 2D1A, 2FX, 2K8)

Int. Cl.: —C 08 d 9/02

## COMPLETE SPECIFICATION

### Plastic Composition

We, DEKALIN DEUTSCHE KLEBSTOFF-WERKE RODIGER & SOHN G.M.B.H., of Hanau/Main, Germany, a German Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a plastic composition capable of sealing cracks, joints or the like

For sealing cracks or faulty joints, especially in automobile construction, but also in the construction of machines and apparatus and structures above and below ground, plastic compositions may be used which consist of mixtures of synthetic plastic materials and advantageously inorganic filler material, such as asbestos, zinc oxide and the like, as well as optionally plasticizers, mineral oil as solvent for the polymer, castor oil for reducing the tackiness and fats or soaps for increasing the tackiness. On supply and when being used, such compositions are plastic and adhere, for example to metal surfaces, because of the tackiness inherent in them. Normally, they are consequently used as an intermediate layer between two metal surfaces. Sealing compositions are known which are based on poly-isobutylene and which remain permanently plastic and also those which harden gradually and in uncontrollable manner after having been used.

A primary object of the present invention is to provide a plastic composition for sealing purposes which has practical advantages and which overcomes or minimises the disadvantages mentioned above.

According to the present invention we provide a plastic composition capable of sealing cracks, joints or the like which comprises a butadiene-acrylonitrile copolymer of a rubber-like character, a hardenable phenol-form-

aldehyde resin and a butadiene-acrylonitrile copolymer in the state of a viscous sticky liquid having a viscosity, measured at 30° C, of 75,000 to 100,000 centipoises. 45

Thus a plastic composition embodying this invention may be formulated which is initially plastic and can be used while in the plastic condition, but then can be stoved at higher temperature and thereby is given a substantially firmer adhesion with a metal than the prior known sealing compositions, and can be so firmly anchored to the metal that it can also be applied freely to the area to be sealed without having to be held by a cooperating surface. Accordingly, such a composition which can be stoved is also suitable for sealing off areas to which access is difficult, for example on a car body, and it can sometimes also be used instead of a soldering or tinning operation, which is substantially more complicated and more costly. As a consequence of the stoving process, the plastic composition becomes somewhat harder, but nevertheless still has a sufficient plasticity which it constantly retains in practice, even when stored for a relatively long period. 50

Preferably the content by weight of butadiene-acrylonitrile copolymer is greater than the phenol-formaldehyde resin content. It is advantageous to use a quantity of phenol-formaldehyde resin such that it guarantees the firm anchoring of the plastic composition to the support after the stoving operation, but that the said composition still remains sufficiently plastic. In principle, any hardenable phenol-formaldehyde resin, such as for example a resol resin, can be considered, but it is preferred to use a resin of the Novolak type, which contains a compound e.g. hexamethylene tetramine, which splits off formaldehyde during the stoving operation. Therefore it is preferred that the plastic composition of this invention should comprise a com- 55

[Price 4s. 6d.]

1,045,577

- 5 pound, e.g. hexamethylene tetramine, capable of splitting off formaldehyde by heating it.
- 10 Apart from the preferred requirement for constant plasticity and firm anchoring after the stoving operation, the composition should desirably also have an adequate tackiness prior to the stoving in order to adhere to sheet metal when it is for example pressed on manually. This can be achieved by including in the plastic composition suitable plasticisers, which have a dissolving action on the rubber-like butadiene-acrylonitrile copolymer, such plasticisers being for example phosphoric acid esters e.g. tricresyl phosphate, or phthalic acid esters e.g. dibutylphthalate. However, the copolymer content of the plastic composition advantageously consists of two different copolymers which are based on butadiene and acrylonitrile, one of the copolymers being a butadiene-acrylonitrile copolymer of a rubber-like character, while the second copolymer is a butadiene-acrylonitrile copolymer in the state of a viscous sticky liquid, which imparts to the plastic composition the desired plasticity and capacity for adhering to metal or the like at room temperature. The first-mentioned rubber-like copolymer preferably has a Mooney viscosity of 73 to 87, advantageously about 83, with an acrylonitrile content of 25 to 40% by weight advantageously 34% by weight. The viscous liquid copolymer preferably has an acrylonitrile content of 25% to 40%, by weight, advantageously about 33% by weight.
- 15 Normally, the plastic composition of this invention will have a content of filler material which may represent a major proportion by weight of the composition. The filler material may be chosen from asbestos fibre, zinc oxide, talc, titanium dioxide, powdered quartz, kaolin and chalk.
- 20 The plastic composition may include a colouring material, for instance carbon black. Flame soot is especially suitable.
- 25 Although the proportions of the constituents in the mixture can be varied within relatively wide limits, it has proved expedient in general practice to use substantially the following proportions by weight:
- 30 10% to 20% of copolymer of butadiene and acrylonitrile with a rubber-like consistency,
- 35 50% to 15% of copolymers of butadiene and acrylonitrile of the type of a highly viscous sticky liquid,
- 40 2% to 8% of phenol-formaldehyde resin with addition of hexamethylene tetramine,
- 45 10% to 15% of plasticiser, especially a phthalic acid ester such as dibutyl phthalate,
- 50 10% to 30% of zinc oxide,
- 55 5% to 30% of asbestos fibres,
- 60 10% to 40% of talc,
- 65 0 to 5% of flame soot.

The phthalic acid ester, which can also be replaced by phosphoric acid ester, serves on the one hand as a plasticiser and on the other hand as a solvent for the phenol-formaldehyde resin.

The following examples are quoted wherein the parts denoted therein are by weight:

EXAMPLE 1.

3.0 parts of phenol-formaldehyde resin are dissolved at a temperature of about 60° C. in 12.0 parts of dibutyl phthalate. The solution is cooled and then there are added thereto 10.0 parts of butadiene-acrylonitrile copolymer with an acrylonitrile content of 33% by weight and a viscosity of about 100,000 centipoises, measured at 30° C., the said copolymer also dissolving.

15.0 parts of rubber-like butadiene-acrylonitrile copolymer with an acrylonitrile content of 34% by weight and a Mooney viscosity of 83 and are initially masticated on a roll mill or preferably in a plunger-type kneader or an internal mixer. Thereafter, 21.0 parts of zinc oxide, 10.0 parts of asbestos fibres, 28.8 parts of talc and optionally 0.2 part of flame soot are supplied with the aforementioned solution to the mixer device and incorporated by mastication until a homogeneous mixture free from lumps has formed. Care has to be taken that the temperature of the sealing composition does not rise higher than 60° to 70° C. during the mastication in order to avoid an initial condensation of the phenol-formaldehyde resin.

The dissolving of the phenol-formaldehyde resin in dibutyl phthalate preferably takes place at a temperature from 50° to 60° C. With the mastication on the roll mill or in the kneader, a temperature of about 60° to 70° C. is positively set. As a result, the synthetic rubber becomes considerably more plastic, whereby the homogeneous mixing in of the fillers is assisted.

EXAMPLE 2

15.0 parts of butadiene-acrylonitrile copolymer with an acrylonitrile content of 34% by weight and a Mooney viscosity of 83,

10.0 parts of butadiene-acrylonitrile copolymer with an acrylonitrile content of 33% by weight and a viscosity of about 100,000 cP, measured at 30° C.

3.0 parts of phenol-formaldehyde resin, 12.0 parts of benzyl butyl phthalate, 11.0 parts of zinc oxide, 30.0 parts of asbestos fibres, 18.8 parts of talc, 0.2 part of flame soot,

100.0

By comparison with the plastic compositions according to Examples 1 and 3 (herein-

70

75

80

85

90

95

100

105

110

115

120

125

5 after quoted) plastic composition according to Example 2 has an even higher degree of tackiness and bonding strength with metal prior to the stoving. Furthermore, after the stoving, it is somewhat softer and more plastic than packings obtained according to Examples 1 and 3.

EXAMPLE 3

10 15.0 parts of butadiene-acrylonitrile copolymer with an acrylonitrile content of 38% by weight and a Mooney viscosity of 83,  
 15.0 parts of butadiene-acrylonitrile copolymer with an acrylonitrile content of 33% by weight and a viscosity of about 100,000 cP, measured at 30° C,  
 3.0 parts of phenol-formaldehyde resin,  
 12.0 parts of dibutyl phthalate,  
 21.0 parts of zinc oxide,  
 10.0 parts of asbestos fibre,  
 28.8 parts of talc,  
 0.2 part of flame soot,  
 100.0.

25 A plastic composition according to the specification given in Example 3 has an even higher resistance to aliphatic oils and benzene than the plastic compositions according to Examples 1 and 2.

30 Since the plastic compositions as exemplified above can best be processed in the form of a packing cord, the previously described compositions are preferably shaped by being forced out of a worm press having a profiled nozzle. The temperature during the extrusion is preferably 40° to 50° C. In order to avoid the separate profiles from sticking together, these can be extruded onto a plastic foil, e.g. of hard polyvinyl chloride, and then reeled or packed in some other manner.

40 If such a sealing or packing cord is laid on a metal surface, e.g. untreated, phosphated, primed or lacquered sheet iron, and is pressed thereon by hand, it has excellent bonding strength with the sheet metal. With suitable heating, such as is usually employed for stoving lacquers or priming compositions, the phenol-formaldehyde resin contained in the plastic composition condenses, with the consequence that the composition experiences a slight hardening and adheres substantially more strongly to the metal sheet. The temperature and duration of the stoving operation are reciprocally dependent on one another.

55 At a temperature of 170° C., the stoving takes for example 30 minutes, whereas 60 minutes are required at a temperature of 135° C.

60 The finally heated packing cord is found to constitute a satisfactory seal between metal components and, as already stated, can in many cases be used instead of a soldering or tinning operation. The plastic composition

after having been heated is found to be resistant to aliphatic oils, benzene and water and is consequently particularly suitable for automobile construction. It is also stable in the temperature range from -35° C. to +90° C. (and for a short time even up to +170° C.) and shows no embrittlement in the cold and only a relatively small increase in the plasticity under heat.

WHAT WE CLAIM IS:—

1. A plastic composition capable of sealing cracks, joints or the like which comprises a butadiene-acrylonitrile copolymer of a rubber-like character a butadiene-acrylonitrile copolymer in the state of a viscous sticky liquid having a viscosity of 75,000 to 100,000 centipoises measured at 30° C. and a hardenable phenol-formaldehyde resin. 75
2. Plastic composition according to claim 1, which comprises filler material. 80
3. Plastic composition according to claim 2, wherein the filler material is chosen from asbestos fibre, zinc oxide, talc, titanium dioxide, powdered quartz, kaolin and chalk. 85
4. Plastic composition according to any preceding claim, which comprises a colouring material. 90
5. Plastic composition according to claim 4, wherein the colouring material is carbon black. 95
6. Plastic composition according to any preceding claim, which comprises a plasticiser. 100
7. Plastic composition according to claim 6, wherein the plasticiser is a phosphoric acid ester or a phthalic acid ester. 105
8. Plastic composition according to claim 7, wherein the plasticiser is tricresyl phosphate or dibutyl phthalate. 110
9. Plastic composition according to any preceding claim, which comprises a compound capable of splitting off formaldehyde by heating it. 115
10. Plastic composition according to claim 9, wherein the said compound is hexamethylene tetramine. 120
11. Plastic composition according to any preceding claim, wherein the content by weight of butadiene-acrylonitrile copolymer or rubber-like character is greater than the phenol-formaldehyde resin content. 120
12. Plastic composition according to any preceding claim, wherein filler material represents a major proportion by weight of the composition. 120
13. A plastic composition according to claim 1 substantially as herein described and exemplified. 120

MEWBURN ELLIS & CO.,  
 Chartered Patent Agent,  
 70 & 72, Chancery Lane,  
 London, W.C.2.  
 Agents for the Applicants.